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(54) GRANULAR WATER-DISPERSIBLE AGENTS AND PROCESS FOR PRODUCING THE SAME

(57) A water dispersible granule formulation prepared by pulverized a part of active ingredients into fine particles under wet milling and pulverized another part of the active ingredients into coarse particles under dry milling, then kneading the both active ingredients for the granulation, and a process for producing the water dispersible granule formulation are disclosed. The water dispersible granule formulation according to the present invention is applicable for production of a water dispersible granule formulation comprising an active ingredient which is easily decomposed owing to environmental conditions and allows to provide the water dispersible granule formulation provided with enhanced initial and residual biological activities.

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Description

Field of Invention

[0001] The present invention is related to a water dispersible granule formulation for an agricultural chemical and a process for producing said water dispersible granule formulation.

Background Art

[0002] Until today, active components to be used as an agricultural chemical having insecticidal, fungicidal or herbicidal activity have been formulated into a wettable powder, an emulsifiable concentrate, a suspension concentrate, dust, etc. and have been used in such a formulation form depending upon the physical and chemical property and the application purpose, However, among the formulation types described above, an emulsifiable concentrate has a problem of environmental pollution caused by organic solvents contained therein, and a suspension concentrate has a problem of easily causing separation of the components into phases during the preservation for a long time since the active ingredient(s) is dispersed in an aqueous solvent used for the formulation. Further, a wettable powder formulation and a powder formulation has a problem in safety for human bodies as they easily cause the dusting at the production process and at the places to practically use them. Due to such problems, several water dispersible granule formulations have been provided recently in order to settle such problems.

[0003] Normally, the water dispersible granule formulation is prepared according to so-called extrusion method, which is combining a solid active ingredient, a carrier comprising minerals in fine powder, surface active agents, etc., pulverizing the combined mixture by using a dry mill, then adding bound water to the mixture and kneading the mixture by using a kneader, and forcibly extruding the kneaded mixture to pass it through a multiporous plate containing a plurality of pores with the diameter of 0.5-2.0 mm.

[0004] However, if the active ingredient has a low melting point, or if the active ingredient has a peculiar property of being hardly pulverized into fine particles, dry milling method has not been applicable for such use.

[0005] In addition, in case of dry milling method, the particle size of the pulverized components in a formulation is normally in a range of from 5 to 20 μm, thus it is difficult to pulverize the components into a size ranging from 3 to 5 μm or less so that there is a problem that the dry milling method cannot be used for the production of the water dispersible granule, particularly when the active ingredient has a low melting point, or the active ingredient is required to be pulverized into fine particles ranging from 3 to 5 μm or less in order to enhance the biological activity.

[0006] Generally, contacting area of an active ingredient with a growing plant gets small when the particle size of the active ingredient is coarse, and the total amount of the active ingredient attached onto vegetable leaves is reduced. For example of an insecticide, the initial insecticidal activity, namely the activity just after the application of the insecticide, may be deteriorated because the penetrating amount of the active ingredient into leaves and the contact frequency between a pest insect and the active ingredient particles on leaves may be generally reduced.

[0007] As a formulation process for resolving the problems as described above, a process to formulate a water dispersible granule is known, where an active ingredient for an agricultural chemical is pulverized into fine particles under wet milling, kneading the ground active ingredient with a carrier consisting of minerals, and granulating the obtained mixture by extrusion, (See, for example, JP laid-open 3-146126 gazette).

[0008] However, when an active ingredient which may be easily decomposed owing to environmental conditions is used for production of a water dispersible granule by kneading the active ingredient with a carrier consisting of minerals following to the wet milling of the active ingredient and then granulating the kneaded product, the residual activity of the active ingredient tends to be remarkably deteriorated due to decomposing effect given by light, water and the like since the particle size of the pulverized active ingredient into fine particles is generally so small as much as 1-5 μm.

[0009] Furthermore, constraint of water supply at the wet milling is imposed due to the required amount of bound water at the kneading, thereby further constraining the amount of the active ingredient to be subjected to the wet milling, which has made hard to produce a water dispersible granule containing high content of the active ingredient.

[0010] Therefore, if the active ingredient is required to be pulverized into fine particles to enhance the biological activity and is the one that is easily decomposed owing to environmental conditions, it is difficult to obtain a water dispersible granule formulation provided with high initial and residual activities according to a conventional process for preparing water dispersible granule formulations.

[0011] Besides, in such cases that (1) a water dispersible granule contains different active ingredients and one of which cannot be pulverized into fine particles by dry milling method, and (2) a water dispersible granule contains different active ingredients, one of which is required to be pulverized into fine particles by wet milling in order to enhance the initial activity, and the other may be pulverized by either wet or dry milling but is required to be pulverized roughly in order to raise the content of the active ingredients in the formulation or enhance the residual activity it was so hard to employ a process of kneading and granulating materials following to dry milling and a process of kneading and

granulating materials following to wet milling for the production of a water dispersible granule formulation.

Disclosure of the Invention

[0012] It is an object of the present invention to provide a water dispersible granule formulation, which can enhance the initial and residual activity of an active ingredient contained in the formulation.

[0013] The present invention firstly provides a water dispersible granule formulation containing the same or different active ingredient(s) workable as an agricultural chemical and having different average particle sizes (particle diameter distribution) from one to another.

[0014] The water dispersible granule formulation according to the present invention is preferably prepared by mixing and granulating the first active ingredient pulverized into fine particles by wet milling and the second active ingredient pulverized by dry milling.

[0015] Further, the average particle size of the first active ingredient is preferably in a range of from 0.5 to 5 μm, and the average particle size of the second active ingredient is preferably in a range of from 3 to 30 μm.

[0016] In the water dispersible granule formulation according to the present invention, the first active ingredient is preferably in solid form and hardly soluble in water and the solubility in water is preferably less than 1,000 ppm.

[0017] As deaignative examples for the first active ingredient, one or more compounds selected from a group consisting of triflumizole, thiuram, fluazinam, anilazine, captan, hexythiazox, benzoximate, tebufenpyrad, ziram, thiophanate methyl, mepanipyrim and N'-cyclopropylmethyloxy-N-phenylacetyl-2,3-difluoromethylbenzamidine may be given.

[0018] As the second active ingredient to be pulverized by dry milling, any compound being in solid state at an ambient temperature and has a melting point higher than 30 °C may be used without limitation, and two or more of such compounds may be used as the second active ingredient.

[0019] The present invention secondary provides a process to produce a water disperaible granule formulation comprising steps of combining the first active ingredient, a dispersing agent and water each in a given amount and then grinding the combined mixture under wet milling, combining the second active ingredient, a fine carrier consisting of minerals and a dispersing agent each in a given amount and then pulverizing under dry milling, and mixing the mixture obtained in the wet milling process and the mixture obtained in the dry milling and then granulating the obtained mixture.

[0020] In the second invention described above, the process to grind under wet milling preferably contains a process to prepare the average particle size of the active ingredient to a range of from 0.5 to 5 μm and the process to pulverize under dry milling preferably contains a process to prepare the average particle size of the active ingredient to a range of from 3 to 30 μm.

[0021] According to the process of the present invention, the following types of water dispersible granule formulations may be provided.

(1) The water dispersible granule formulation comprising the first active ingredient which is required to be pulverized into fine particles for enhancement of the initial biological activity and cannot be pulverized into fine particles by the dry milling due to the own peculiar property and the second active ingredient which is required to be pulverized into coarse particles for enhancement of the residual activity and to increase the content in the formulation, wherein the first and the second active ingredients may be the same or different with each other.

(2) The water dispersible granule formulation, wherein the first and the second active ingredients are the same, which is provided with highly-effective initial biological activity and highly-effective residual activity by means of pulverizing the part of the active ingredient into fine particles by means of the wet milling and of pulverizing the remainder into coarse particles by means of the dry milling.

(3) The water dispersible granule formulation, wherein the first and the second active ingredients are different with each othen the first active ingredient that cannot be pulverized by the dry milling due to the own peculiar property is pulverized into fine particles by means of the wet milling, and the second active ingredient that is required to be pulverized into coarse particles or of which content is required to be increased to enhance the residual activity is pulverized by means of the dry milling.

Preferred Embodiments for the Invention

[0022] Now, the present invention is explained in detail in the following.

[0023] The present invention is (1) to provide a water dispersible granule formulation provided with highly-effective initial and residual activities comprising the first and the second active ingredients both workable as an agricultural chemical and are the same compound, which is provided with highly-effective initial biological activity and residual activity by preparing the particle size of both active ingredients different with each other by means of wet milling and dry milling, and (2) to provide a water dispersible granule formulation comprising the first and the second active ingre-

dient both workable as an agricultural chemical and are different compounds with each other, wherein the first active ingredient is required to be pulverized into fine particles by means of wet milling in order to enhance its initial biological activity or if it cannot be pulverized by means of dry milling due to the own peculiar property, and the second active ingredient can be pulverized into coarse particles by either wet milling or dry milling but is required to be pulverized in order to enhance its residual activity or to increase its content in the formulation.

[0024] The first active ingredient contained in the water dispersible granule formulation according to the present invention is preferably in solid state at an ambient temperature and hardly soluble in water, and more preferably, the active ingredient has solubility in water of 1,000 ppm or less.

[0025] As designative examples for the first active ingredient describe above, one or more compounds selected from a group consisting of triflumizole, thiuram, fluazinam, anilazine, captan, hexythiazox, benzoximate, tebufenpyrad, ziram, thiophanate methyl, mepanipyrim and N'-cyclopropylmethyloxy-N-phenylacetyl-2,3-difluoro-6-trifluoromethyl-benzamidine may be given.

[0026] As the second active ingredient to be contained in the water dispersible granule formulation according to the present invention, any compound being in solid state at an ambient temperature and has a melting point higher than 30 °C may be used without limitation, and two or more of such compounds may be combined, and the similar ones as exampled above for the first active ingredient may be used as the second active ingredient as well.

[0027] The first feature of the present invention is directed to the difference in the average particle sizes of the plural active ingredients, or particle size distribution in other word, respectively obtainable by wet milling and dry milling. Consequently, a compound as the first active ingredient and a compound as the second active ingredient to be used may be the same or different with each other.

[0028] In the present invention, as examples for the dispersing agent to be combined at the wet milling, polyoxyethylene, polyoxypropylene, copolymer of polyoxyethylene and polyoxypropylene, sodium alkylbenzenesulfonate, alkylphosphoric ester added with polyoxyethylne, aliphatic amines added with polyoxyethylene, aliphatic alcohols added with polyoxyethylene, tween-type surface active agent of sorbitanmonooleate, sorbitantrioleate and the like added with polyoxyethylene, span-type surface active agent of sorbitanmonooleate, sorbitantrioleate and the like, castor oil ester added with polyoxyethylene, tristyrylphenyl ether or distyrylphenyl ether added with polyoxyethylene, tristyrylphenyl ether phosphate added with polyoxyethylene, distyrylphenyl ether sulfate added with polyoxyethylene, alcohol ether added with polyoxyethylene, sodium alkylnaphthahenesulfionate, sodium laurylsulfate, sodium ligninsulfonate, formaldehyde condensate of sodium alkylnaphthalenesulfonate, formaldehyde condensate of sodium phenolsulfonate, copolymer of isobutylene and maleic anhydride, and sodium polycarboxylate may be given, and two or more of the exampled compounds described above may be used in a combination as the dispersing agent.

[0029] As examples for the dispersing agent to be combined at the dry milling, sodium alkylnaphthalenesulfonate, sodium alkylbenzenesulfonate, sodium laurylsulfate, sodium ligninsulfonate, formaldehyde condensate of sodium alkylnaphthalenesulfonate, aldehyde condensate of sodium phenolsulfonate, copolymer of isobutylate and maleic anhydride, sodium polycarboxylate, sodium dioctylsulfosuccinate, higher alcohol sulfuric ester sodium and the like may be given, and two or more of the compounds exampled above may be used in combination as the dispersing agent.

[0030] As examples for the fine carrier consisting of minerals to be combined at the dry milling process, an inorganic salt, such as potassium chloride, calcium carbonate, ammonium sulfate, potassium phosphate and sodium phosphate, diatomaceous earth, bentonite, pyrophilite-type clay and caolinite-type clay may be given, and two or more of the compounds exampled above may be used in combination as the carrier.

[0031] In addition, silicon series surfactants, sodium and calcium salts of a higher fatty acid, the mixture thereof acetylene-type surfactants, and the like may be added to the water dispersible granule formulation to reduce foaming at the wet milling and at the dilution process.

[0032] The contents of each components in the water dispersible granule formulation according to the present invention differ depending on the type of the active ingredient, however, as a ratio relative to the total formulation, the content of the active ingredient in total is in a range of 0.02-90 wt%, and preferably in a range of 0.02-70 wt%, and the amounts of the active ingredient to be contained at the wet milling process and at the dry milling may be arbitrary varied. The amount of the dispersing agent to be added at the wet milling is in a range of 1-10 wt%, and preferably in a range of 1-5 wt%, and the amount of the dispersing agent to be added at the dry milling is in a range of 1-30 wt%, and preferably in a range of 5-20 wt%. The amount of the carrier comprising fine powder minerals is in a range of 1-50 wt%, and preferably in a range of 10-40 wt%, and the amount of the anti-foaming agent is less than 5 wt% and is preferably less than 3 wt%.

[0033] The water dispersible granule formulation, hereinafter might be abbreviated as WDG, of the present invention is produced as explained below.

(1) An active ingredient, a dispersing agent and an anti-foaming agent are dissolved in water, dispersed and then pulverized into fine particles under wet milling to prepare a suspension to be used for the water dispersible granule formulation, said suspension hereinafter might be abbreviated as WDG-SC.

(2) An active ingredient, a dispersing agent and a carrier comprising fine powder minerals are mixed and pulverized under dry milling process to prepare wettable powder to be used for the water dispersible granule formulation, said wettable powder might be abbreviated as WDG-WP.
(3) The obtained WDG-SC is added to the WDG-WP, and the resulting mixture is added with bound water, kneaded by using a kneader, and passed through multiporous plate containing pores each of which diameter is ranging from 0.5 to 2.0 mm to obtain granulated moist mixture in noodle-like shape, and the granulated mixture is dried by using an appropriate dryer to obtain the objective water dispersible granule formulation.

[0034] As a granulation method, any method may be employed if it has been used in producing granular formulation for an active ingredient for plant protection use. As examples for the granulation method, extrusion, agitation, breaking, fluid bed, spray dryer, etc. may be given. The particle size and the appearance of the granular formulation may be arbitrary modified depending upon the objective use, such as the type of an active ingredient and the dilution process.

Examples:

[0035] Now, the present invention is further described in detail with referring the examples in the following, however, it should be noted that the scope of the present invention is not limited to the description in the examples, and the first and the second active ingredients, various types of additives, and the combination ratio may be modified without limitation as far as the modification does not exceed the scope of the subject matter of the present invention.

Example 1

[0036] N'-cyclopropylmethyloxy-N-phenylacetyl-2,3-difluoro-6-trifluoromethylbenzamidine, (hereinafter designated as "compound A"), in an amount of 100g, tristyrylphenyl ether added with polyoxyethylene of which HLB being 15 more or less in an amount of 10g, sodium polycarboxylate in an amount of 10g and a silicon series anti-foaming agent in an amount of 2.5g were mixed and added with distilled water in an amount of 150g, and the resulting mixture was dissolved and dispersed by using polytron. The dispersed mixture was then pulverized into fine particles under wet milling wherein zircon beads with a diameter of 1 mm are used by using Eiger motor mill (manufactured by EIGER JAPAN Co. Ltd.) to prepare the WDG-SC of the compound A having the average particle size of 1.5 μ m.
[0037] Then, triflumizole in an amount of 100g, sodium alkylnaphthalenesulfonate in an amount of 10g, formaldehyde condensate of sodium alkylnaphthalenesulfonate in an amount of 140g, sodium ligninsulfonate in an amount of 80g, diatomaceous earth in an amount of 300g and potassium chloride in an amount of 237.5g were mixed and then pulverized into coarse particles under dry milling to prepare the WDG-WP containing triflumizole, wherein the average particle size of particles containing triflumizole is 7 μm.
[0038] To the obtained WDG-WP in am amount of 877.5g, the WDG-SC (272,5g) obtained above and distilled water (180g) were added, and the resulting mixture was then kneaded by using Bench Kneader (manufactured by Irie Shokai Co. Ltd.), granulated into moist granular product in noodle-like shape with a diameter of 0.6 mm by using micro-type granule preparation apparatus (manufactured by Tsutsui Rikagaku Kikai Co., Ltd.) and dried at 40°C for 12 hours by using a blowing drier to prepare the WDG (WDG-1) of the Example 1.

Example 2

[0039] The compound A in an amount of 100g, distyrylphenyl ether added with polyoxyethylene of which HLB being 15 more or lees in an amount of 10g, sodium polycarboxylate in an amount of 10g and silicon series anti-foaming agent in an amount of 2.5g were mixed and added with distilled water in an amount of 150g, and the resulting mixture was pulverized into fine particles under wet milling according to the same procedure as described in the Example 1 to prepare the WDG-SC of the compound A having the average particle size of 3.0 μm.
[0040] Then, triflumizole in an amount of 300g, sodium alkylnaphthalenesulfonate in an amount of 10g, sodium alkylbenzenesulfonate in an amount of 10g, formaldehyde condensate of sodium alkylnaphthalenesulfonate in an amount of 140g, sodium ligninsulfonate in an amount of 80g, diatomaceous earth in an amount of 200g and potassium chloride in an amount of 137.6g were mixed and then pulverized into coarse particles according to the same process as described in the Example 1 to prepare the WDG-WP containing triflumizole, wherein the average particle size of particles containing triflumizole is 6 μm.
[0041] Then, the obtained WDG-WP in an amount of 877.5g was added with the WDG-SC in an amount of 272.6g and distilled water in an amount of 150g, and the resulting mixture was processed according to the procedure as described in the Example 1 to prepare the WDG (WDG-2) of the Example 2.

Example 3

[0042] The compound A in an amount of 150g, tristyrylphenyl ether added with polyoxyethylene of which HLB being 15 more or less in an amount of 10g, sodium polycarboxylate in an amount of 10g and silicon series anti-foaming agent in an amount of 2.5g were mixed and then added with distilled water in an amount of 125g, and the resulting mixture was pulverized into fine particles under wet milling according to the same procedure as described in the Example 1 to prepare the WDG-SC containing the compound A having the average particle size of 1.5 μm.

[0043] Then, thiophanate methyl in an amount of 600g, sodium alkylnaphthalenesulfonate in an amount of 10g, formaldehyde condensate of sodium alkylnaphthalenesulfonate in an amount of 50g, sodium ligninsulfonate in an amount of 25g, calcium carbonate in an amount of 100g and potassium chloride in an amount of 42.5g were mixed and then pulverized into coarse particles under dry milling according to the same procedure as described in the Example 1 to prepare the WDG-WP containing thiophanate methyl of which particles having the average particle size of 7 μm.

[0044] To the obtained WDG-WP in an amount of 827.5g, the WDG-SC in an amount of 297.5g and distilled water in an amount of 75g were added to obtain the WDG (WDG-3) of the Example 3 according to the same procedure as described in the Example 1.

Example 4

[0045] Triflumizole in an amount of 100g, block copolymer of polyoxyethylene of which HLB being 14 more or less and polyoxypropylene in an amount of 50g, formaldehyde condensate of sodium phenolsulfonate in an amount of 70g and silicon series anti-foaming agent in an amount of 2.5g were mixed and then added with distilled water in an amount of 200g, and the resulting mixture was pulverized into fine particles under wet milling according to the same procedure as described in the Example 1 to prepare the WDG-SC containing triflumizole of which average particle size being 5.0 μm.

[0046] Then, thiophanate methyl in an amount of 600g, sodium alkylnaphthalenesulfonate in an amount of 10g, formaldehyde condensate of sodium alkylnaphthalenesulfonate in an amount of 25g, sodium ligninsulfonate in an amount of 25g, calcium carbonate in an amount of 100g and potassium chloride in an amount of 17.5g were mixed and then pulverized into coarse particles under dry milling according to the same procedure as described in the Example 1 to prepare the WDG-WP containing thiophanate methyl of which particles having the average particle size of 7 μm.

[0047] To the obtained WDG-WP in an amount of 777.5g, the WDG-SC in an amount of 422.5g and distilled water in an amount of 30g were added to obtain the WDG (WDG-4) of the Example 4 according to the same procedure as described in the Example 1.

Example 5

[0048] Triflumizole in an amount of 100g, tristyrylphenyl ether added with polyoxyethylene of which HLB being 15 more or less in an amount of 10g, sodium polycarboxylate in an amount of 10g and silicon series anti-foaming agent in an amount of 2.5g were mixed and then added with distilled water in an amount of 150g, and the resulting mixture was pulverized into fine particles under wet milling according to the same procedure as described in the Example 1 to prepare the WDG-SC containing triflumizole of which average particle size being 2 μm.

[0049] Then, triflumizole in an amount of 200g, sodium alkylnaphthalenesulfonate in an amount of 20g, sodium alkylbenzenesulfonate in an amount of 10g, formaldehyde condensate of sodium alkylnaphthalenesulfonate in an amount of 140g, sodium ligninsulfonate in an amount of 80g, diatomaceous earth in an amount of 300g and potassium chloride in an amount of 127.5g were mixed and then pulverized into coarse particles under dry milling according to the same procedure as described in the Example 1 to prepare the WDG-WP of which particles containing triflumizole having the average particle size of 8 μm.

[0050] To the obtained WDG-WP in an amount of 877.5g, the WDG-SC obtained above in an amount of 272.5g and distilled water in an amount of 180g were added, and the resulting mixture was kneaded by using Bentch Kneader (manufactured by Irie Shokai Co., Ltd.) and granulated into the moist noodle-shaped product having the diameter of 0.6 mm by using a micro-type granules preparation apparatus (manufactured by Tsutsui Rikagaku Kikai Co., Ltd.) and dried at 40°C for 12 hours by using a blowing dryer to obtain the WDG (WDG-5) of the Example 5.

Example 6

[0051] Thiophanate methyl in an amount of 100g, tristyrylphenyl ether added with polyoxyethylene of which HLB being 15 more or less in an amount of 10g, sodium polycarboxylate in an amount of 10g and silicon series anti-foaming agent in an amount of 2,5g were mixed and then added with distilled water in an amount of 150g, and the resulting mixture was pulverized into fine particles under wet milling according to the same procedure as described in the Ex-

ample 1 to prepare the WDG-SC containing triflumizole of which average particle size being 2 μm.

[0052] Then, thiophanate methyl in an amount of 600g, sodium alkylnaphthalenesulfonate in an amount of 10g, formaldehyde condensate of sodium alkylnaphthalenesulfonate in an amount of 50g, sodium ligninsulfonate in an amount of 25g, calcium carbonate in an amount of 100g and potassium chloride in an amount of 92,5g were mixed and then pulverized into coarse particles under dry milling according to the same procedure as described in the Example 1 to prepare the WDG-WP of which particles containing thiophanate methyl having the average particle size of 7 μm.

[0053] To the obtained WDG-WP in an amount of 877.5g, the WDC-SC obtained above in an amount of 272.5g and distilled water in an amount of 150g were added to obtain the WDG (WDG-6) of the Example 6 according to the same procedure as described in the Example 1.

[0054] The compositions of the formulations obtained in the examples described above are shown in Table 1.

Table 1

Example	1	2	3	4	5	6
WDG-SC						
Compound A	100	100	150			
Triflumizole				100	100	
Thiophanate methyl						100
POE trismylphenyl ether	10		10		10	10
POE distyrylphenyl ether		10				
POE-POP block copolymer				50		
Formaldehyde condensate of Sodium phenolsulfonate				70		
Sodium polycarboxylate	10	10	10		10	10
Silicon-containing defoaming agent	2.5	2.5	2.5	2.5	2.5	2.5
Distilled water	150	150	125	200	150	150
Average particle size (μm)	1.5	3.0	1.5	5.0	2.0	2.0
WDG-WP						
Triflumizole	100	300			200	
Thiophanate methyl			600	600		600
Sodium alkylnaphthalenesulfonate	10	10	10	10	20	10
Sodium alkylbenzenesulfonate	10	10			10	
Sodium ligninsulfonate	80	80	26	25	80	25
Formaldehyde condensate of Sodium naphthalenesulfonate	140	140	50	25	140	60
Diatomaceous earth	300	200		200	300	
Calcium carbonate			100	100		100
Potassium chloride	237.5	137.5	42.5	17.5	127,5	92.5
Average particle size (μm)	7.0	6.0	7.0	7.0	8.0	7.0
POE: Polyoxyethylene, POP: Polyoxypropylene						

[0055] The formulation examples for the water dispersible granule according to the present invention, which can be prepared in the same manner as the examples described above, are shown in Table 2.

[0056] The water to be contained in the WDG-SC is required to make the pulverized mixture into fine particles under wet milling in slurry state and the amount might be selected in a range of from 100 to 300g. The particle size of the active ingredient in the WDG-SC may be adjusted depending on the objective for the use. The amount of water to be added after the mixing of the WDG-WP and the WDG-SC into the mixture is required to be appropriate for making the kneaded product in argillaceous state.

Table 2

Example	7	8	9	10	11	12
WDG-SC						
Clethoxim methyl	100					
Mepanipyrim		100	200			
Thiuram				100		
Hexythiazox					100	150
POE tristyrylphenyl ether	10	10	10			10
Sodium polycarboxylate	10	10	10		20	
POE-POP block copolymer				50		20
Formaldehyde condensate of Sodium phenolsulfonate				70		50
Sodium alkylnaphthalenesulfonate					20	
WDG-WP						
Triflumizole	300					
Thiophanate methyl		600	500			
Acetamiprid					300	400
Fluazinam				200		
Sodium alkylnaphthalenesulfonate	20	10	10	20	20	10
Sodium ligninsulfonate	100	25	25	80	80	100
Formaldehyde condensate of Sodium naphthalenesulfonate	200	50	50	150	80	100
Calcium carbonate	200	100	100			
Diatomaceous earth				200		
Clay					200	100
Ammonium sulfate				130		
Potassium chloride	60	95	95		180	60

Industrial Use:

[0057] Now, the advantageous effect of the present invention is explained in the following with referring the comparative examples and the comparative test examples with the examples described above.

Comparative Example 1 (Same composition as Example 1, but the active ingredient is pulverized into fine particles under wet milling together with other components.)

[0058] The compound A in an amount of 100g, triflumizole in an amount of 100g, tristyrylphenyl ether added with polyoxyethylene of which HLB being 15 more or less in an amount of 10g, sodium polycarboxylate in an amount of 10g and silicon series anti-foaming agent in an amount of 2.5g were mixed and then added with distilled water in an amount of 300g, and the resulting mixture was pulverized into fine particles under wet milling according to the same procedure as described in the Example 1 to prepare the WDG-SC containing the active ingredient of which average particle size being 1.5 μm.

[0059] Then, sodium alkylnaphthalenesulfonate in an amount of 10g, sodium alkylbenzenesulfonate in an amount of 10g, formaldehyde condensate of sodium alkylnaphthalenesulfonate in an amount of 140g, sodium ligninsulfonate in an amount of 80g, diatomaceous earth in an amount of 300g and potassium chloride in an amount of 237.5g were mixed and then pulverized into fine particles under dry milling according to the same procedure as described in the Example 1 to prepare a powder formulation of which particles having the average particle size of 7 μm.

[0060] To the obtained powder formulation in an amount of 777.5g, the WDG-SC obtained above in an amount of 522.5g and distilled water in an amount of 30g were added to obtain the WDG (WDG-comparison 1) of the Comparative Example 1 according to the same procedure as described in the Example 1.

Test Example 1

[0061] The two types of WDG each in an amount of 1g, the WDG (WDG-1) prepared in the Example 1 and the WDG (WDG-comparison 1) prepared in the Comparative Example 1, were separately added into 100 ml tap water and were dispersed while shaking. 1 ml of the obtained dispersion was placed into a petri dish with a diameter of 9 cm and dried at an ambient temperature. Then, the dispersion was exposed to sunlight (approximately 100,000 lux) and the remaining amount of the compound A on the petri dish was determined at a fixed interval by means of HPLC analysis. The remaining ratio of the compound A based on the amount of triflumizole before exposing to sunlight is shown in Table 3.

Table 3

Sunlight Irradiation Time (hr)	WDG-1	WDG-comparison 1
0	100%	100%
3	96%	67%
6	89%	44%

[0062] From the Table 3, it is demonstrated that the water dispersible granule formulation prepared according to the Example 1 is stable against sunlight and can show excellent residual activity in comparison with the WDG prepared in the Comparative Example 1.

Comparative Example 2 (Example of the WDG containing the same active ingredient as one in the Example 2 prepared by dry milling)

[0063] The compound A in an amount of 100g, triflumizole in an amount of 300g, sodium alkylnaphthalenesulfonate in an amount of 20g, formaldehyde condensate of sodium alkylnaphthalenesulfonate in an amount of 140g, sodium ligninsulfonate in an amount of 100g, calcium carbonate in an amount of 200g and potassium chloride in an amount of 140g were mixed and then pulverized under dry milling according to the same procedure as described in the Example 1. However, the part of the compound A was not pulverized well and the particles having the particle size being larger than several hundreds μm remained in the pulverized powder, and therefore, it was not successful to prepare the water dispersible granule according to this process.

Comparative Example 3 (Example of the WDG containing the same active ingredient as one in the Example 3 prepared by dry pulverization)

[0064] The compound A in an amount of 150g, thiophanate methyl in an amount of 600g, sodium alkylnaphthalenesulfonate in an amount of 10g, formaldehyde condensate of sodium alkylnaphthalenesulfonate in an amount of 50g, sodium ligninsulfonate in an amount of 25g, calcium carbonate in an amount of 100g and potassium chloride in an amount of 65g were mixed and then pulverized under dry milling according to the same procedure as described in the Example 1. However, the part of the compound A was not pulverized well and the particles having the particle size being larger than several hundreds μm remained in the pulverized powder, and therefore, it was not successful to prepare the water dispersible granule according to this process.

Comparative Example 4 (Example of WDG containing the same active ingredient as one in the Example 4 prepared by wet grinding)

[0065] Triflumizole in an amount of 100g, thiophanate methyl in an amount of 600g, block copolymer of polyoxyethylene of which HLB being 14 more or less and polyoxypropylene in an amount of 50g, formaldehyde condensate of sodium phenolsulfonate in an amount of 70g, tristyrylphenyl ether added with polyoxyethylene of which HLB being 15 more or less in an amount of 10g and silicon series anti-foaming agent in an amount of 2.5g were mixed and then added with distilled water to be required for preparing the WDG-SC, then the total amount of the mixture came to 700g. The mixture was then pulverized under wet milling to prepare the WDG-SC containing the active ingredient having the average particle size of 5 μm.

[0066] Then, the WDG-SC was mixed with calcium carbonate in an amount of 100g and potassium chloride in an amount of 67.5g, and the mixture was pulverized under dry milling to prepare a powder formulation of which particles having the average particle size of 5 μm.

[0067] To the obtained powder formulation, the WDG-SC obtained above in an amount of 1,532.5g was added, however, the resulting mixture was not prepared into argillaceous state during the kneading process due to the presence of excessive water since the water amount in the WDG-SC exceeded the required water amount for the preparation of the WDG, which accordingly make unable to prepare the moist noodle-shaped product for granulation, and therefore, it was not successful to prepare the water dispersible granule according to this process.

Comparative Example 5 (WDG containing triflumizole of which particle size being 2 μm)

[0068] Triflumizole in an amount of 100g, trisyrylphenyl ether added with polyoxyethylene of which HLB being 15 more or less in an amount of 10g, sodium polycarboxylate in an amount of 10g and silicon series anti-foaming agent in an amount of 2.5g were mixed and then added with distilled water in an amount of 150g, and the resulting mixture was pulverized under wet milling according to the same procedure as described in the Example 1 to prepare the WDG-SC containing the active ingredient having the average particle size of 2 μm.

[0069] Then, sodium alkylnaphthalenesulfonate in an amount of 20g, sodium alkylbenzenesulfonate in an amount of 10g, formaldehyde condensate of sodium alkylnaphthalenesulfonate in an amount of 140g, sodium ligninsulfonate in an amount of 80g, diatomaceous earth in an amount of 300g and potassium chloride in an amount of 327.5g were mixed and then pulverized under dry milling according to the same procedure as described in the Example 1 to prepare the powder formulation of which particles having the average particle size of 8 μm. The obtained powder formulation was then added with the WDG-SC obtained above in an amount of 272.5g and distilled water in an amount of 200g to prepare the WDG (WDG-comparison 5) of the Comparative Example 5 according to the same procedure as described in the Example 1.

Comparative Example 6 (WDG containing triflumizole with the average particle size of 8 μm)

[0070] Triflumizole in an amount of 300g, sodium alkylnaphthalenesulfonate in an amount of 20g, sodium alkylbenzenesulfonate in an amount of 10g, formaldehyde condensate of sodium alkylnaphthalenesulfonate in an amount of 140g, sodium ligninsulfonate in an amount of 80g, diatomaceous earth in an amount of 300g and potassium chloride in an amount of 150g were mixed, and the mixture was pulverized under dry milling to prepare the WG-WP of which particles containing triflumizole having the average particle size of 8 μm. The obtained WG-WP in an amount of 1,000g was added with distilled water in an amount of 240g to prepare the WDG (WDG-comparison 6) of the Comparative Example 6 according to the same procedure as described in the Example 1.

Test Example 2

[0071] Each of WDG containing triflumizole prepared in the Example 5 (WDG-5) and the Comparative Examples 5 and 6 (WDG-comparison 5 and WDG-comparison 6) was separately diluted at a predetermined concentration and was sprayed to apple fruits. After naturally drying the sprayed apple fruits, the spore suspension of apple scab fungus (spore concentration, 1 x 10^5/ml) was sprayed onto the apples on 0 and 3 days after spraying of the WDG. On 11 days later, the appearance of the infection by apple scab fungus was accessed, and the disease control efficacy in the plots sprayed with the WDG was evaluated in comparison with the plot without spraying of the WDG according to the equation presented below. The results are shown in Table 4. The preventive effect (initial activity) may be known from the effectiveness when the inoculation of the spore suspension was made just after the spraying of the WDG (0 day) and the residual effect may be known from the effectiveness when the inoculation of the spore suspension was made on 3 days after the spraying of the WDG.

Disease Control Efficacy = (1 - (Area covered by scab fungus infection on the WDG-sprayed apples / Area covered by scab fungus infection on apples without spray of the WDG)) x 100

Table 4

Formulation	Concentration of Active Ingredient Sprayed (ppm)	Disease Control Efficacy (%)	
		Preventive effect (Initial activily)	Residual effect
WDG-5	50	100	100
	12	100	20
	3	95	0
WDG-comparison 5	50	100	75
	12	100	0
	3	90	0
WDG-comparison 6	50	100	100
	12	100	12
	3	50	0

[0072] As shown in the Table 4, the water dispersible granule formulation (WDG-5) prepared in the Example 5 showed excellent residual effectiveness in comparison with the corresponding formulation (WDG-comparison 5) prepared in the Comparative Example 5 and excellent initial effectiveness in comparison with the formulation (WDG-comparison 6) prepared in the Comparative Example 6.

Comparative Example 7 (WDG containing thiophanate methyl with the average particle size of 2 μm)

[0073] Thiophanate methyl in an amount of 100g, tristyrylphenyl ether added with polyoxyethylene of which HLB being 15 more or less in an amount of 10g, sodium polycarboxylate in an amount of 10g and silicon series anti-foaming agent in an amount of 2.5g were mixed and the mixture was then added with distilled water in an amount of 150g, and the resulting mixture was pulverized under wet milling according to the same procedure as described in the Example 1 to prepare the WDG-SC containing the active ingredient with the average particle size of 2 μm.

[0074] Then, sodium alkylnaphthalenesulfonate in an amount of 10g, formaldehyde condensate of sodium alkylnaphthalenesulfonid acid in an amount of 100g, sodium ligninsulfonate in an amount of 25g, calcium carbonate in an amount of 100g and potassium chloride in an amount of 115g were mixed, and the resulting mixture was pulverized under dry milling according to the same procedure as described in the Example 1 to prepare the powder formulation of which particles having the average particle size of 7 μm. The obtained powder formulation in an amount of 877.5g was added with the above-obtained WDG-SC in an amount of 272.5g and distilled water in an amount of 180g to obtain the WDG of the Comparative Example 7 (WDG-comparison 7) according to the same procedure as described in the Example 1.

Comparative Example 8 (WDG containing thiophanate methyl with the average particle size of 7 μm)

[0075] Thiophanate methyl in an amount of 700g, sodium alkylnaphthalenesulfonate in an amount of 10g, formaldehyde condensate of alkylnaphthalenesulfonic acid in an amount of 50g, sodium ligninsulfonate in an amount of 25g, calcium carbonate in an amount of 100g and potassium chloride in an amount of 115g were mixed, and the resulting mixture was pulverized under dry milling to prepare the WDG-WP of which particles having the average particle size of 7 μm. The obtained WDG-WP in an amount of 1,000g was added with distilled water in an amount of 300g to prepare the WDG of the Comparative Example 8 (WDG-comparison 8) according to the same procedure as described in the Example 1.

Test Example 3

[0076] Each of WDG containing thiophanate methyl prepared in the Example 6 (WDG-6) and the Comparative Examples 7 and 8 (WDG-comparison 7 and WDG-comparison 8) was separately diluted at a predetermined concentration and the dilution was sprayed to sugarbeet plants (variety; Monohomare). After naturally drying the sprayed sugarbeet plants, the spore suspension of Cercospora leaf spot fungus (spore concentration, 1 x 10^5/ml) was sprayed onto the sugarbeet plants on 0 and 7 days after spraying of the WDG. On 11th day after the spraying, the appearance of the

infection by Cercospora leaf spot fungus was accessed, and the disease control efficacy in the plots sprayed with the WDG was evaluated in comparison with the plot without spraying of the WDG according to the equation presented in the Test Example 1. The results are shown in Table 5. The preventive effect (initial activity) may be known from the effectiveness when the inoculation of the spore suspension was made just after the spraying of the WDG (0 day) and the residual effect may be known from the effectiveness when the inoculation of the spore suspension was made on 7 days after the spraying of the WDG.

Table 5

Formulation	Concentration of Active Ingredient Sprayed (ppm)	Disease Control Efficacy (%)	
		Preventive Effect (Initial Activity)	Residual Effect
WDG-6	200	100	100
	50	100	85
	12	100	0
	3	80	0
WDG-comparison 7	200	100	95
	50	100	20
	12	100	0
	3	82	0
WDG-comparison 8	200	100	100
	50	100	82
	12	75	0
	3	19	0

[0077] In the Table 5, the water dispersible granule formulation (WDG-6) prepared in the Example 6 showed excellent residual effectiveness in comparison with the corresponding formulation (WDG-comparison 7) prepared in the Comparative Example 7 and excellent initial effectiveness in comparison with the formulation (WDG-comparison 8) prepared in the Comparative Example 8.

[0078] As explained above, the present invention is directed to a process for producing a water dispersible granule formulation for agricultural chemical use, particularly comprising an active ingredient easily decomposed owing to environmental conditions, which is suitable for preparing a water dispersible granule formulation, wherein the active ingredient is required to be pulverized into fine particles in order to enhance the initial biological activity and is also required to be pulverized into coarse particles in order to enhance the residual activity. According to the present invention, the part of the active ingredients may be pulverized into fine particles under wet milling, and the other part of the active ingredients may be pulverized into coarse particles under dry milling, then kneading the both active ingredients to prepare the granules containing the both active ingredients, thereby allowing to simply and efficiently produce a water dispersible granule containing different types of particles having different particle sizes, respectively.

Claims

1. A water dispersible granule formulation containing either same or different types of active ingredients each having different distribution in the particle size from one to another.

2. A water dispersible granule formulation according to claim 1 **characterized in that** the formulation is produced by mixing and granulating the first active ingredient pulverized under wet milling and the second active ingredient pulverized under dry milling.

3. A water dispersible granule formulation according to claims 1 and 2 wherein the average particle size of the first active ingredient is in a range of from 0.5 to 5 μm.

4. A water dispersible granule formulation according to any of claims 1 through 3 wherein the average particle size of the second active ingredient is in a range of fiom 3 to 30 μm.

5. A water dispersible granule formulation according to any of claims 1 through 4 wherein the first active ingredient is a compound being solid at an ambient temperature and hardly soluble in water.

6. A water dispersible granule formulation according to any of claims 1 through 5 wherein the first active ingredient is a compound being solid at an ambient temperature and having the solubility in water of 1,000 ppm or less.

7. A water dispersible granule formulation according to any of claims 1 through 6 wherein the first active ingredient (s) is one or more selected from a group consisting of triflumizole, thiuram, fluazinam, anilazine, captan, hexythiazox, benzoximate, tebufenpyrad, ziram, thiophanate methyl, mepanipyrim, clethoxim methyl, triazine and N'-cyclopropylmethyloxy-N-phenylacetyl-2,3-difluoro-6-trifluoromethylbenzamidine.

8. A process for producing a water dispersible granule formulation comprising a step to combine the first active ingredient, a dispersing agent and water each in a predetermined amount and to pulverize the combined mixture into fine particles under wet milling, a step to combine the second active ingredient, a fine carrier consisting of minerals and a dispersing agent each in a predetermined amount and to pulverize the combined mixture under dry milling and a step to admix the mixture obtained in the wet milling step and the mixture obtained in the dry milling step and to granulate the admixed mixture.

9. Aprocess according to claim 8 wherein the wet milling process contains a step to adjust the average particle size of the first active ingredient in a range of from 0.5 to 5 μm.

10. Aprocess according to claims 8 and 9 wherein the dry milling process contains a step to adjust the average particle size of the second active ingredient in a range of from 3 to 30 μm.

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl[7] A01N25/12, A01N43/50, A01N47/26, A01N43/40, A01N43/66, A01N47/04, A01N47/28, A01N37/52, A01N47/34, A01N43/54, A01N37/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl[7] A01N25/12, A01N43/50, A01N47/26, A01N43/40, A01N43/66, A01N47/04, A01N47/28, A01N37/52, A01N47/34, A01N43/54, A01N37/50

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	JP, 63-66101, A (Kao Corporation), 24 March, 1988 (24.03.88), especially, page 9, table 2 (Family: none)	1 2-10
X A	JP, 53-50333, A (Hattori Kogyo K.K.), 08 May, 1978 (08.05.78), especially, page 3, production example-1 (Family: none)	1 2-10
X A	JP, 40-16587, B1 (Toshiyasu SATO), 29 July, 1965 (29.07.65), especially, page 1, right column, tables (Family: none)	1 2-10
X A	JP, 3-120201, A (SANKYO COMPANY, LIMITED), 22 May, 1991 (22.05.91), especially, page 4, lower right column, lines 11-13 (Family: none)	1 2-10
X A	EP, 141509, A2 (SUMITOMO CHEMICAL COMPANY, LIMITED), 15 May, 1985 (15.05.85), especially, page 6, Example 2	1 2-10

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

International application No.
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	& JP, 60-64904, A	
A	WO, 97/46093, A1 (Nippon Soda Co., Ltd.), 11 December, 1997 (11.12.97) & JP, 10-500426, A	1-10
A	JP, 3-146126, A (SANKYO COMPANY, LIMITED), 21 June, 1991 (21.06.91) (Family: none)	1-10

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